

SPECIFICATION

COMPOSITE PAPYRACEOUS MATERIAL

Technical Field

[0001] The present invention relates to a composite papyraceous material comprising a fibrous polyimide and a fibrous polytetrafluoroethylene (PTFE).

Background Art

[0002] Various papyraceous materials containing a high-performance engineering plastic as a fiber component were proposed and expected to be used widely, for example, as members in electronic devices such as board material and heat-resistant structural materials. Among them, the one containing a fluoroplastic fiber as a constituent, which is advantageous in dielectric and friction properties etc. has been studied intensively.

[0003] For example, Patent Document 1 proposes a papyraceous material made of a fluoroplastic fiber and a heat-resistant engineering plastic fiber.

[0004] Patent Document 2 proposes a sheet insulator made of a base fiber material, mixture of an insulation fiber and a fluoroplastic fiber, impregnated with an impregnating agent.

[0005] Patent Document 3 proposes a low-dielectric printed-wiring-board material in combination of a mixed nonwoven fabric of a fluoroplastic fiber and a heat-resistant engineering plastic fiber with a cyanate resin.

[0006] Patent Document 4 proposes a fluorine resin composition in combination of a polytetrafluoroethylene resin for sliding purpose and a polyimide fiber.

[0007] As for papyraceous materials containing a polyimide fiber as a constituent, for example, Patent Document 5 proposes a base nonwoven fabric for laminated boards, in which the polyimide fibers are bonded with a thermosetting binder.

[0008] However, the fluoroplastic fibers used in Patent Documents 1 to 3 have the shape of chopped strand substantially, and the fiber diameter thereof is significantly larger than that of pulp-shaped fibers if compared by the same weight, causing some concern about uniformity when the fibers are used in combination with other materials. In addition, the fluorine fibers used are sufficiently burned in the manufacturing process of the fluoroplastic fiber, and thus, do not function sufficiently as a binder for binding fibers with each other. It is inevitable to blend a binder component to produce a sheet product in a wet process. In many cases, the binder component added causes deterioration of the properties of

the papyraceous material obtained.

[0009] Although the shape etc. of the polytetrafluoroethylene resin in Patent Document 4 are not specified and are still unknown, it seems practically impossible to prepare a thin paper-shaped composite product, considering the manufacturing process.

[0010] In addition, a thermosetting resin is used as a binder of the polyimide fiber in Patent Document 5. As described above, it is only possible to prepare a papyraceous material having the properties inherent to polyimide fiber impaired by such a thermosetting resin.

Patent Document 1: Japanese Patent Laid-Open No. 10-212686

Patent Document 2: Japanese Patent Laid-Open No. 11-144529

Patent Document 3: Japanese Patent No. 2762544

Patent Document 4: Japanese Patent No. 2983900

Patent Document 5: Japanese Patent Laid-Open No. 11-200210

Disclosure of Invention

Technical Problems to be Solved

[0011] An object of the present invention, which was made in the background of the conventional technology, to provide a papyraceous material made of an engineering plastic fiber that is superior in strength, thermal dimensional stability, chemical resistance, and abrasion resistance and has unprecedented small values of water

absorption and dielectric property.

[0012] Specifically, the present invention relates to a composite papyraceous material comprising a fibrous polyimide and a fibrous polytetrafluoroethylene.

[0013] The fibrous polyimide is not particularly limited, but preferably a fiber prepared, for example, by melt spinning of a thermoplastic polyimide resin and cut to a particular length, preferably a short fiber; particularly preferably a crystalline fiber.

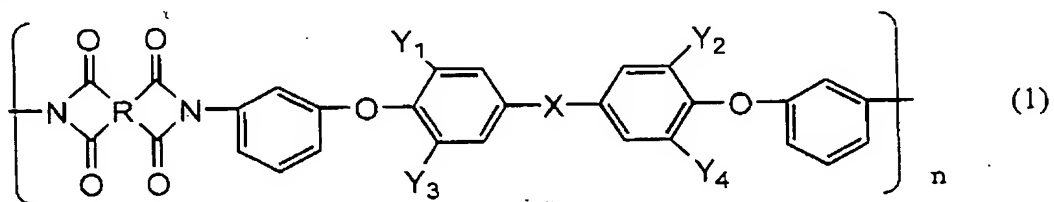
[0014] The thermoplastic polyimide preferably has a glass transition temperature of 230°C or higher and a melting point of 400°C or lower. A glass transition point of lower than 230°C is not favorable, as it makes the fiber less heat resistant. On the other hand, a melting point of higher than 400°C is unfavorable, as it makes thermal processing more difficult.

[0015] Considering uniformity of a resulting composite papyraceous material, the fibrous polyimide is preferably a short fiber, and the average fiber length thereof is 1 to 15 mm, preferably 2 to 8 mm, and the average fiber diameter thereof is 3 to 30 μm , preferably 4 to 20 μm .

[0016] It is possible to enhance orientation in the crystalline region of the filament obtained, for example, by melt spinning of a crystalline thermoplastic polyimide resin, by heat stretching under a suitable condition. The

fibrous polyimide highly oriented in the crystalline region, which shows a smaller dimensional change during heating or cooling, improves the thermal dimensional stability of the resulting papyraceous material, has smaller water absorption, and thus, is extremely resistant to the change in dimension and electrical characteristic by water absorption. The "crystalline fiber" is defined by the crystallinity of fibrous polyimide, and preferably has a crystallinity of 15% or more, preferably 20% or more, particularly preferably 25% or more, as determined by X-ray diffractometry. The crystallinity of less than 15% is unfavorable as it leads to increase in thermal dimensional change and water absorption.

[0017] For satisfying the properties above, the polyimide is a polyimide having the chemical structure represented by the following General Formula (1) as its repeating unit:

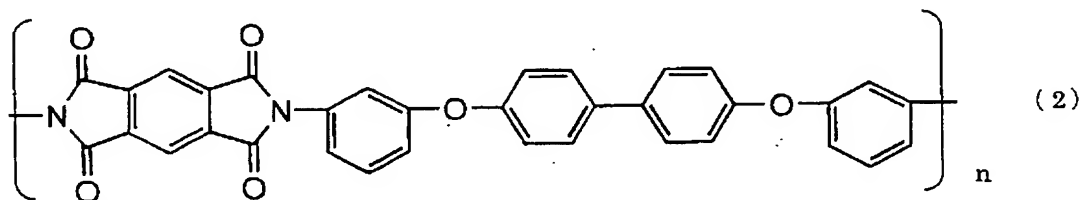


(wherein R represents a quadrivalent aromatic residue selected from monocyclic aromatic groups, condensed polycyclic aromatic groups, and uncondensed polycyclic aromatic groups in which the aromatic rings are bound to

each other directly or via a crosslinking group; X represents a direct bond or a bivalent residue selected from hydrocarbon groups, a carbonyl group, an ether group, a thio group or a sulfonyl group; and Y_1 to Y_4 respectively represent a hydrogen or halogen atom or a monovalent residue selected from an alkyl group or an alkoxyl group).

Among the polyimides, the polyimide represented by the General Formula (1) wherein R is a monocyclic aromatic group is more preferably; X is a direct bond is more preferable; and each of Y_1 to Y_4 is a hydrogen atom is more preferable.

[0018] Favorable typical examples of the polyimides include polyimides having the following Chemical Formula (2) as the repeating unit:



(wherein n is preferably 5 to 200).

Such a polyimide is commercially available, for example, as Aurum (trade name, manufactured by Mitsui Chemicals Inc.).

[0019] During preparation of polyimide fibers, another polyimide having a different chemical structure may be blended; and another polymer such as polyester, polyolefin,

polyamide, polyphenylene sulfide, polyether imide, and polyether ether ketone, or fluoro-resin, as well as an inorganic filler such as titanium oxide, zinc oxide, magnesium oxide, alumina, silica, aluminum nitride, silicon nitride, boron nitride, silicon carbide, carbon black, graphite, or mica may be blended so far as the properties required for the polyimide and the papyraceous material used in the present invention are not impaired.

[0020] The fibrous polytetrafluoroethylene for use in the present invention is fibrous powder in shape. The fibrous powder of polytetrafluoroethylene is preferably prepared, for example, by beating polytetrafluoroethylene powder, and such a fibrous powder has ununiform whisker-like branches and yet a fibrous shape as a whole, but shows a phenomenon as powder at the visual level. The fibrous powder preferably has an average fiber length of 5 to 2,000 μm and an average shape factor of 5 or more. The powder having these values lower than the above ranges leads to decrease in water filtering property and productivity in the paper making step and only gives a paper lower in air permeability. The fibrous powder having these values higher than the above ranges leads to deterioration in the paper surface state and makes it difficult to produce thin uniform paper. In addition the fibrous powder preferably has a specific surface area, as determined by nitrogen

absorption method, of $4.0\text{m}^2/\text{g}$ or more. The fibrous powder having a lower specific surface area is inferior in binding efficiency, and thus, the papyraceous material obtained has a lower strength. The average shape factor is a value obtained by dividing fiber length by fiber width.

[0021] The polytetrafluoroethylene may be a tetrafluoroethylene homopolymer or a copolymer of tetrafluoroethylene with a trace amount of monomer other than tetrafluoroethylene that is non-processable by melting (hereinafter, referred to as modified polytetrafluoroethylene).

Examples of the trace amount monomers include perfluoroolefins, perfluoro(alkylvinylether)s, cyclic fluorinated monomers, perfluoroalkylethylenes, and the like.

Examples of the perfluoroolefins include hexafluoropropylene and the like; examples of the perfluoro(alkylvinylether)s include perfluoro(methylvinylether), perfluoro(propylvinylether), and the like; examples of the cyclic fluorinated monomers include fluorodioxol, and the like; and examples of the perfluoroalkylethylenes include perfluoromethylethylene and the like.

[0022] The fibrous polytetrafluoroethylene is preferably a partially baked polytetrafluoroethylene having a low temperature-sided peak area ratio of 88.5% or more with

respect to the total peak area in the melting endothermic curve, as determined by differential scanning calorimetry (DSC) analysis at a programmed heating rate of 5°C per minute. Such a fibrous polytetrafluoroethylene gives a papyraceous material having smoother surface and superior in air permeability. The upper limit is preferably 99.0%. A low temperature-sided peak area ratio lower than the range above makes it difficult to prepare a surface-smooth paper, while that higher than the range above gives a papyraceous material unfavorably structured and drastically lower in usability.

[0023] The peak area obtained by differential scanning calorimetry is proportional to the quantity of heat and generally to the number of the molecules in sample in an allowable range. Thus, the ratio of disentangled polytetrafluoroethylene molecules can be evaluated with a peak ratio of the area of low temperature-sided peaks to the total peak area obtained by differential scanning calorimetry. A double peak or a single peak having a distinct shoulder may be considered mathematically as a master curve of three or more multiple normal-distribution curves, but it is sufficiently reasonable to separate the peak having two vertexes into two normal-distribution or similar curves, and such an assumption gave adequate results also in evaluation of the present invention.

Accordingly, it is possible to assume that partially disentangled molecules are also included in the normal distribution curve of undisentangled molecules in evaluation, because the quantity of heat needed for disentanglement is smaller.

[0024] The combined absorption peak can be separated normally by approximation with using Gaussian-Lorentian curve. The Gaussian-Lorentian curve characteristically has a smaller deviation than either Gaussian curve or Lorentian curve, and most of calculation software installed in commercial analyzers employs this method. In the present invention, basic peak positions are determined, by supplying two apparent vertexes of the raw polytetrafluoroethylene powder as the initial values and making approximation without restricting. The basic peak positions thus obtained, for example, of the fibrous polytetrafluoroethylene used in Example 1 of the present invention are 339.14°C and 343.01°C; and a combined curve was separated into two curves and the peak areas thereof were obtained by performing approximation using these values as standards while restricting only the peak temperatures to temperatures lower by 0.6 to 0.7°C than the initial values but not restricting the linear half-value widths. In the evaluation above, information on the raw powder was used for shortening the period needed for value

convergence, but the values may also be determined directly from the melting curve of fibrous powder.

[0025] The composite papyraceous material according to the present invention is prepared as a paper-shaped composite in combination of the fibrous polyimide and the polytetrafluoroethylene described above. The composite-forming method is not particularly limited, but the composite can be prepared easily in a paper-making process, as the raw materials are blended. Among many paper-making methods, application of a wet paper-making method is preferable, for production of a thin composite papyraceous material having a uniform formation.

[0026] The wet paper-making method include a dispersion step of dispersing at least fibrous polytetrafluoroethylene in water, a mixing step of mixing fibrous polyimide, a paper-making, and a drying step.

[0027] In the dispersion step, a slurry of fibrous polytetrafluoroethylene is obtained by adding the fibrous polytetrafluoroethylene in water and defibrating it in a pulper, refiner, or the like equipped with agitator. Normally, polytetrafluoroethylene has a great contact angle with water and it is hard to disperse it in water uniformly, and thus, it is preferable to add a dispersant previously to the fiber or fibrous powder or to blend it in the water for dispersion. The dispersant for use is not particularly

limited, but preferably a nonionic polyoxyethylene alkylethers, because it is effective for dispersion even when added in a small amount.

[0028] In the mixing step of mixing the fibrous polyimide, a mixed slurry is prepared by adding fibrous polyimide to the slurry of fibrous polytetrafluoroethylene obtained in the dispersion step and processing in a manner similar to the dispersion step. The fibrous polyimide is normally dispersible in the slurry uniformly without use of a dispersant.

[0029] The blending ratio of fibrous polyimide to polytetrafluoroethylene may be determined properly according to applications, but the lower limit value in blending ratio of the fibrous polyimide is 5 percent by mass, preferably 10 percent by mass. The upper limit ratio is 90 percent by mass, more preferably 80 percent by mass. A fibrous polyimide blending ratio of less than 5 percent by mass may lead to insufficient thermal dimensional stability and strength, while a ratio of more than 90 percent by mass to insufficient handling efficiency in the production process, and insufficient strength and dielectric property of composite papyraceous material.

[0030] Then, a papyraceous material (paper-made product) is prepared through a paper-making step of sheet-making the mixed slurry in a known wet papermaking machine such as

cylinder wet paper machine, short-screen wet paper machine, inclined short-screen wet paper machine or inclined fourdrinier wet paper machine, and the obtained paper-made product is put into a drying step of drying it in a hot-air, contact or radiant dryer installed close to the paper machine. Thus, a composite papyraceous material is obtained. It is possible to bond the fibrous polytetrafluoroethylene to the fibrous polyimide under compression and give a composite papyraceous material superior in shape stability, when a pressurization step of applying a pressure onto the paper-made product in the thickness direction by nip rolls or a pair of metal rolls, is provided in the paper making process. The pressurization may be performed at room temperature; the pressure is normally, approximately 1 to 10kgf/cm; but of course, a pressure may be applied under heat if possible. The pressurization step may be placed between the paper-making step and the drying step or after the drying step.

[0031] The paper-making process is controlled to make the papyraceous material after drying have a basis weight of 50 to 1,500 g/m², preferably 100 to 1,200 g/m². The basis weight of less than that leads to deterioration in easiness in handling in papermaking process, making it difficult to make paper reliably. The greater basis weight may lead to notable problems in production such as decrease

in filtered water in the paper-making step and insufficient drying.

[0032] Then, the composite papyraceous material thus prepared is pressurized under heat in the thickness direction in a heat-pressurizing apparatus such as a roll-pressing machine having a pair of metal rolls such as calendering rolls or a double belt-pressing machine having a pair of facing metal belts etc.; and the fibrous powder of polytetrafluoroethylene is fused on the fibrous polyimide, drastically increasing the strength of the composite papyraceous material. That is, a composite papyraceous material having fibrous powder of polytetrafluoroethylene fused on fibrous polyimide, i.e., a densified composite papyraceous material, is obtained by the processing in the step of preparing a composite papyraceous material by the wet paper making method and additionally in the step of heat-pressurizing the papyraceous material obtained. Needless to say, the heat-pressurization step may be performed continuously after the paper-making step or separately in another line.

[0033] The heating temperature during the heat pressurization is preferably not lower than the melting point of polytetrafluoroethylene. A final heating temperature of lower than the melting point may result in insufficient improvement in mechanical strength property.

It also means that it is possible to keep the binding force in a particular range until the final heating step if the papyraceous material is heat-treated at a temperature of lower than the melting point and to obtain processed goods such as laminate by using such an intermediate. The heating temperature is preferably not higher than the melting point of the polyimide for the fibrous polyimide, and if the polyimide is a crystalline polyimide, the heating temperature is preferably lower than the melting point of the polyimide and more preferably lower by 10°C or more than the melting point. A heating temperature of higher than the melting point of the polyimide is undesirable, because it leads to significant fusion of the fibrous polyimide and insufficient blending effects by the fibrous polyimide. The heating temperature is normally, approximately 340 to 380°C. The melting point is a value obtained by using a differential scanning calorimeter (Pyris1 DSC, manufactured by PerkinElmer Co., Ltd.).

[0034] The pressure during heat pressurization is not particularly limited, but a higher applied pressure leads to a lower porosity and densification of the composite papyraceous material obtained, and thus, for example, a pressure of approximately 0.05 to 10 MPa may be applied.

[0035] Pressurization under heat of two or more sheets of the composite papyraceous material according to the

present invention in the step above gives a densified composite papyraceous material without interlayers, and thus, it is possible to prepare a densified papyraceous material having a desired thickness by changing the number of the sheets used. It is also possible then to prepare a composite papyraceous material in which the composition of polyimide and polytetrafluoroethylene varies in the thickness direction, by using the composite papyraceous materials according to the present invention different in the composition in respective layers.

[0036] The thickness of the papyraceous material thus obtained is determined according to the basis weight in the paper-making step and the number of sheets used in lamination and the degree of densification during heat pressurization, but preferably 20 to 2,000 μm , more preferably 25 to 800 μm , from the points of application, productivity, and uniformity in physical properties. The thickness of smaller than the lower limit leads to deterioration in the easiness of handling and lower yield in the production process, while the thickness of greater than the upper limit tends to give only papyraceous materials lower in dimensional uniformity in the heat-pressurization step. The apparent density thereof is preferably 0.3 to 2.1 g/cm^3 , and the density of lower than the range may lead to deterioration in strength, while the

density higher than that to practical difficulty of production.

[0037] The composite papyraceous material according to the present invention may contain various additives in the range that does not impair the advantages of the present invention. Examples of the additives include short fibers or pulps of other organic or inorganic material, i.e., short fibers or pulps such as of aramide, polyester, polyether imide, polyether ether ketone, polysulfone, polyphenylene sulfide, polyketone, carbon, glass, and alumina; and various particulate matters (fillers) such as titanium oxide, zinc oxide, magnesium oxide, alumina, silica, aluminum nitride, silicon nitride, boron nitride, silicon carbide, carbon black, graphite, mica, and molybdenum disulfide; and the like.

[0038] For improvement in strength etc., a thermoplastic resin, for example a polyimide resin or the precursor thereof, or a thermosetting resin, for example an epoxy resin or the like, may be added according to applications. In such a case, the polyimide resin or the precursor thereof or the epoxy resin or the like is normally used in the emulsion or solution state for coating, spraying or impregnation.

[0039] One or more of these additives may be added in an amount that does not impair the advantage of the present

invention, the total mass after drying preferably remains 30 percent by mass or less with respect to the total mass of the composite paper according to the present invention, for preserving various favorable properties.

[0040] As described above, the composite papyraceous material according to the present invention may be processed into the state in which the fibrous powder of polytetrafluoroethylene is fused and bonded to the fibrous polyimide in the heat-pressurization step, and such a densified papyraceous material has a superior strength. In addition, such a papyraceous material, even when laminated in the heat-pressurization step, does not show a phenomenon of breakage from the interlayer during use and retains a strength at a substantially same level as that of a single-layer papyraceous material. The strength thereof is determined by the blending ratio of fibrous powder of polytetrafluoroethylene to fibrous polyimide, the degree of densification, or the amount of the third component blended, but, for example, the average breaking length, as determined according to the test method specified by JIS-P8113, is normally in the range of 0.5 to 7 km.

[0041] The composite papyraceous material according to the present invention is resistant to thermal dimensional change and superior in dimensional stability when used at high temperature. As for the dimensional stability, both

the average linear expansion coefficients at 20 to 230°C in the production and width directions of the composite papyraceous material are preferably in the range of -20 to 30 $\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$ (as determined according to JIS-K7197). The average linear expansion coefficient outside the region of -20 to 30 $\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$ may lead to increase in the dimensional stability when used at high temperature and make the papyraceous material unsuitable for use.

[0042] In the present invention, it is possible to prepare a papyraceous material superior in dimensional stability and its directional balance, by preparing a papyraceous material wherein the fibrous polyimide and the polytetrafluoroethylene described above are dispersed randomly.

[0043] The composite papyraceous material preferably has lower water absorption, and in a preferred embodiment of the present invention, the water absorption, as calculated according to the following formula when left in an environment at 25°C and a relative humidity 60% for 24 hours, is preferably 0.5% or less.

[0044]

$$\text{Water absorption} = \frac{W - W_0}{W_0} \times 100(\%) \quad (\text{Formula I})$$

(wherein W represents mass of nonwoven fabric after moisture absorption, and W_0 represents mass of nonwoven

fabric when absolutely dried).

[0045] Generally, polyimides are known to have a relatively higher water absorption because of the strong polarity of the imide groups therein, and the molded products thereof often had problems of the change in dimension and electrical characteristic after absorption of moisture. Papyraceous materials of conventional amorphous polyimide fibers also had the problem in dimensional change by water absorption; but in the present invention, it is possible to prepare a high-performance composite papyraceous material lower in water absorption than ever, by using a crystalline polyimide fiber and a fibrous powder of polytetrafluoroethylene lower in water absorption as the main components. In particular, the polyimide represented by Chemical Formula (1) or (2) has crystallinity and a low imide-group content in the chemical structure, and thus, has especially lower water absorption among polyimides; and from these viewpoints, use of the fibrous polyimide above is preferable.

[0046] Both polyimide and polytetrafluoroethylene have a lower dielectric constant and are superior in insulating performance. The papyraceous material according to the present invention does not contain a third component as a binder, and thus, the composite papyraceous material thereof can be given the same properties as above. The

electric properties can be evaluated at room temperature and 2.45 GHz by using a cylindrical dielectric constant meter (constituted of a resonator manufactured by Kanto Electronics Application & Development Inc. and a network analyzer manufactured by Agilent Technologies). The dielectric constant of the composite papyraceous material according to the present invention may vary according to the content ratio of fibrous polyimide to fibrous powder of polytetrafluoroethylene and the apparent density of composite papyraceous material, but the dielectric constant of a densified composite papyraceous material as determined by the test method above is normally in the range of 2.0 to 3.1. The dielectric loss, as determined similarly, is in the range of 1×10^{-5} to 3×10^{-3} .

[0047] Polyimide and polytetrafluoroethylene are known to be superior both in chemical and oxidation resistances, and the composite papyraceous material according to the present invention is also superior in these properties. The chemical resistance can be evaluated by determining the change in weight, color, and shape after a composite papyraceous material is immersed in a test chemical at room temperature for a week; for example, large change in weight and dimension is observed when it corroded significantly with the chemical, and some increase in weight is observed when it swells therein; and the composite papyraceous

material according to the present invention is known to be resistant to many common polar solvents such as alcohol solvents, ether solvents, ketone solvents, ester solvents, and amide solvents, and nonpolar solvents such as hydrocarbon solvents, and various oils and fuels. The oxidation resistance can be evaluated by determining the deterioration of the composite papyraceous material by oxidation when it is immersed in the so-called Fenton reagent, i.e., a hydrogen peroxide solution containing a small amount of an activation agent such as iron sulfate (III); and the composite papyraceous material according to the present invention showed almost no deterioration when immersed therein, for example, at 70°C for 48 hours.

[0048] The composite papyraceous material according to the present invention, which has a structure wherein polyimide superior in abrasion resistance and polytetrafluoroethylene superior in lubricity are dispersed uniformly, is superior in frictional abrasion resistance. For example, it can be evaluated by using a thrust frictional abrasion tester (EMFIII-E, manufactured by Toyo Baldwin) at room temperature without use of a lubricant, and the composite papyraceous material according to the present invention, shows a favorable abrasion resistance when it is slid in contact with a counter material of SUS material or aluminum material under pressure at a constant

sliding velocity for 48 hours and does not damage the counter material.

[0049] The composite papyraceous material according to the present invention, which has all the properties described above, is a raw material most favorably used in products that demand strength, heat resistance, and thermal dimensional stability such as seamless belt, stamping mold, guard tube, flame-resistant papyraceous material, valve sheet, solder pattern paper and cushioning material. It is also superior in electrical characteristics and thus may be applied to a circuit board. It is also superior in chemical and abrasion resistances and thus, it is a raw material favorable as filter, paper material for polishing, electrolyte film, and sealing material.

[0050] Hereinafter, the present invention will be described with reference to Examples.

[0051] (Production Example of fibrous polyimide)

The polyimide resin used was Aurum (trade name: manufactured by Mitsui Chemicals Inc.). The polyimide resin was melted at 415°C and extruded through a nozzle of 0.2 mm in diameter into a strand, which was drawn at a velocity of 700 m/min, solidified by cooling, and wound around a paper jointing tube, to give a fibrous polyimide having a fiber diameter of approximately 23 μm . Then, the fibrous polyimide was drawn in a heater at 350°C

approximately thrice, to give a fibrous polyimide having a fiber diameter of approximately 12 μm . The fibrous polyimide obtained had a crystal orientation increased by stretching. In this Example, short fiber prepared by cutting the fibrous polyimide to a length of 5 mm was used. The crystallinity of the short fiber was 26%, and the melting point was 389°C.

[0052] (Production Example of fibrous polytetrafluoroethylene powder)

A polymer obtained by emulsion polymerization of 100 mol % of tetrafluoroethylene was used as a raw polytetrafluoroethylene powder (average diameter: 570 μm). The raw polytetrafluoroethylene powder obtained was fed into a hopper by a feeder. Then, the polytetrafluoroethylene powder was fed, assisted with dry air as needed, into a stretching tank equipped with a rotating blade (inner tank diameter: 160 mm ϕ) and stretched therein. Part of the bottom face of the stretching tank had a mesh structure, and the powder having a diameter smaller than a particular size was allowed to be discharged from the stretching tank. The powder was processed with a standard classification screen, while removing the powder having a diameter of 5 μm or less, to give a raw fibrous polytetrafluoroethylene powder.

[0053] The fibrous polytetrafluoroethylene powder

obtained had:

an average fiber length of 1.5 μm ;

an average shape factor of 40;

a specific surface area of 6.38 m^2/g ; and

a low temperature-sided peak area ratio of 92.3%.

[0054] (Example 1)

To an aqueous dispersion containing 0.1 part by weight of a polyoxyethylene alkylether in 1,000 parts by mass of water, added was 3.2 parts by mass of the fibrous polytetrafluoroethylene powder; and the mixture was agitated in an agitating machine (pulper), to give a uniform dispersion.

[0055] Then, 0.8 part by mass of the polyimide short fiber cut to 5 mm in length was added to the dispersion, and the mixture was agitated to give a slurry in which respective raw materials were mixed and dispersed uniformly.

[0056] The slurry was diluted with water additionally to be a slurry concentration of 0.02 percent by mass, and fed into an inclined continuous short-screen paper machine, to give a paper-made product. The paper-made product obtained had a water content of approximately 30 percent by mass.

[0057] Then, the fibrous polytetrafluoroethylene powder and the polyimide short fiber were adhered to each other under a linear pressure of 0.1 N/mm by using nip rolls equipped with a pair of stainless steel rolls at room

temperature.

[0058] The resultant was fed into and dried in a conveyor-type hot air dryer attached to the paper machine, to give a composite papyraceous material having a water content of approximately 0 percent by mass.

[0059] The composite papyraceous material obtained had a favorable strength and shape stability because the fibrous polytetrafluoroethylene powder was bonded under pressure to the fibrous polyimide; and the fibrous polyimide and the fibrous polytetrafluoroethylene powder were dispersed and blended uniformly. The papyraceous material obtained through the above processes was designated as a composite papyraceous material A.

[0060] The composite papyraceous material A obtained by the wet paper making method above was preheated at 240°C for 2 minutes under no pressure in a continuous belt-pressing machine (manufactured by Sandvik), heated at 350°C for 5 minutes under a pressure of 25 N/mm, and then, cooled rapidly to 50°C under the same pressure, to give a densified composite papyraceous material continuously. The composite papyraceous material obtained, in which the fibrous polytetrafluoroethylene powder was melted and bonded to the polyimide short fiber surface, had a smooth surface and a densified structure. The densified papyraceous material obtained through the above processes

was designated as a composite papyraceous material B.

[0061] The composite papyraceous material B obtained had a basis weight of 256 g/m^2 and a thickness of $154 \text{ }\mu\text{m}$. The average linear expansion coefficient, breaking length, water absorption, and dielectric constant thereof were also determined. The results are summarized in Table 1.

[0062] The thickness was determined as an average of the 50 thicknesses measured at an interval of one point in 100 cm^2 ($10 \times 10 \text{ cm}$) by using a digital thickness gage.

The breaking length was determined according to JIS-P8113 by using a universal tester (manufactured by Intesco).

The average linear expansion coefficient was determined according to JIS-K7197 by using a TMA measuring apparatus (TMA2940, manufactured by TA Instruments).

The water absorption was determined according to the General Formula I.

The dielectric constant was determined according to the method of using the cylindrical dielectric constant meter described above. The test sample used was a rod-shaped product of 1.4 mm square prepared by densifying the laminated composite papyraceous materials A to a thickness of 1.4 mm in a similar manner to the composite papyraceous material B and cutting the densified product into pieces of 1.4 mm width.

[0063] (Examples 2 to 5)

A composite papyraceous materials B were prepared in a manner similar to Example 1, except that the blending ratio of the fibrous polyimide to the fibrous polytetrafluoroethylene powder was changed to the value shown in Table 1. Various physical properties of the composite papyraceous materials obtained are summarized in Table 1.

[0064] (Comparative Example 1)

A composite papyraceous material A of the polyimide short fiber was prepared in a manner similar to Example 1, except that no fibrous polytetrafluoroethylene powder was used and the polyimide short fiber was added in an amount of 4 parts by mass.

[0065] In the papyraceous material obtained in Comparative Example 1, which contains no fibrous polytetrafluoroethylene powder, the fibers are not bonded under pressure to each other and thus, the product did not have paper-like shape, and it was not possible to obtain a favorable papyraceous material A.

[0066] (Comparative Example 2)

A papyraceous material B of the fibrous polytetrafluoroethylene powder was prepared in a manner similar to Example 1, except that no polyimide short fiber was used and the fibrous polytetrafluoroethylene powder added in an amount of 4 parts by mass. Various physical

properties of the composite papyraceous material B obtained are summarized in Table 1.

[0067] (Comparative Example 3)

A composite papyraceous material A was prepared in a manner similar to Example 1, except that a polytetrafluoroethylene short fiber having an average fiber length of 5 mm (trade name: Toyofron, manufactured by Toray Fine Chemicals Co. Ltd.) was used instead of the fibrous polytetrafluoroethylene powder.

The polytetrafluoroethylene short fiber used in the Comparative Example had:

an average shape factor of 250

a specific surface area of $0.1 \text{ m}^2/\text{g}$, and

a low temperature-sided peak area ratio of 100%.

[0068] In this Comparative Example, the fibers are not bound under pressure to each other probably because the polytetrafluoroethylene short fiber did not function as a binder sufficiently, and thus, it was not possible to obtain a favorable paper-like shape and to obtain a satisfactory papyraceous material A.

[0069]

	PI ¹⁾ (Part by mass)	PTFE ²⁾ (Part by mass)	Basis weight (g/m ²)	Thickness (μ m)	Average expansion coefficient (μ m/m°C)	Water absorption (%)	Breaking length (km)	Dielectric constant
Example 1	0.8	3.2	256	154	-1.5	0.1	2.1	2.15
Example 2	1.6	2.4	260	182	-4.7	0.1	4.1	2.34
Example 3	2.4	1.6	249	227	-4.8	0.2	5.6	2.35
Example 4	3.2	0.8	268	274	-3.6	0.3	5.6	2.36
Example 5	0.4	3.6	294	162	20	0.1	1.3	2.10
Comparative example 1	4.0	0	—	—	—	—	—	—
Comparative example 2	0	4.2	220	100	168	0.0	0.3	1.95
Comparative example 3	0.8	3.2	—	—	—	—	—	—

1) Fibrous polyimide ; 2) Polytetrafluoroethylene

[0070] (Evaluation of oxidation resistance)

(Example 6)

The composite papyraceous material B obtained in Example 2 and cut into pieces of 100 mm in length and 10 mm in width was used as a sample. The sample was immersed and left in an oxidizing agent solution prepared by dissolving iron sulfate (II) to a concentration of 20 ppm in an aqueous 30 percent by mass hydrogen peroxide solution at 70°C for 80 hours. Then, the sample was removed, washed with water, and dried, and the breaking length thereof was determined.

[0071] The breaking length of the sample immersed in the oxidizing agent solution relative to 100% of the breaking

length of the sample immersed in pure water instead of the oxidizing agent solution and processed similarly was used as an indicator of the oxidation resistance. As a result, the composite papyraceous material B had a high oxidation resistance of 95%. It is useful as a base material for electrolyte films, for example, in polymer electrolyte fuel cell, that demand high oxidation resistance.

[0072] (Comparative Example 4)

A composite papyraceous material B was prepared in a manner similar to Example 2, except that the polyimide short fiber was replaced with an aramide fiber having a fiber diameter of approximately 15 μm and an average fiber length of 6 mm (trade name: Twaron, manufactured by Japan Aramid).

[0073] The basis weight of the composite papyraceous material obtained was 296 g/m²; the thickness, 295 μm ; and the breaking length, 1.9 km. The oxidation resistance of the composite papyraceous material B obtained, as determined similarly to Example 6, was 63%, indicating that the composite papyraceous material was inferior in oxidation resistance.

[0074] (Evaluation of sliding property)

(Example 7)

Two composite papyraceous materials A obtained in Example 1 and cut to 500×500 mm in size were heated to

350°C under 3 MPa pressure and additionally at 350°C for 15 minute under the same pressure by using a pressing machine having a pressurizing plate equipped with a heating apparatus, to give a densified composite papyraceous material.

[0075] The density of the composite papyraceous material obtained was 1.60 g/m^2 , and the thickness was 322 μm . A sliding test was performed by using the composite papyraceous material and cut to a size of 30×30 mm as a test sample and a carbon steel S45C jig having a sliding face of a ring-shaped cross section having an outer diameter 25 mm and an inner diameter 20 mm as a counter material, in a frictional abrasion tester (EMFIII-E, manufactured by Toyo Baldwin). The surface roughness R_a of the sliding face of the counter material was 0.5 μm , and the test was performed without use of a lubricant. The abrasion amount and the friction coefficient of the sample were determined after slid at peripheral velocity of 100 m/minute, pressure of 0.49 MPa, and normal temperature for 20 hours. The abrasion amount was evaluated with the change in weight of the sample between before and after the test. The friction coefficient was calculated from the stress (torque) generated in the rotation direction of the sample during measurement, as determined by the load cell attached to the apparatus. The results obtained are

summarized in Table 2.

[0076] (Comparative Example 5)

A composite papyraceous material A was prepared in a manner similar to Example 1, except that an aramide fiber having a fiber diameter of approximately 15 μm and an average fiber length of 6 mm (trade name: Twaron; manufactured by Japan Aramid) was used instead of the polyimide short fiber. Then, two composite papyraceous materials A were laminated in a manner similar to Example 7, to give a composite papyraceous material. The density of the composite papyraceous material obtained was 1.45 g/m^2 , and the thickness was 353 μm . The composite papyraceous material obtained was evaluated in the sliding test, similarly to Example 7. The results obtained are summarized in Table 2.

[0077]

	Density (g/cm^3)	Thickness (μm)	Abrasion amount (mg)	Friction coefficient
Examples 7	1.60	322	0.9	0.20
Comparative example 5	1.45	353	3.1	0.23

[0078] As apparent from Table 2, the composite papyraceous materials according to the present invention are superior in sliding property and resistant to abrasion even under high sliding conditions, and have a smaller friction coefficient.